APPLICATION FOR UNITED STATES LETTERS PATENT

FOR

BORON FREE AUTOMOTIVE GEAR OIL

Inventors: Chip Hewette
Jeffrey L. Milner

Assignee: Ethyl Petroleum Additives, Inc.

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TECHNICAL FIELD OF THE INVENTION

The present invention is in the field of lubricant additives and lubricant formulations. Specifically, the present invention relates to a boron-free lubricant additive package that is capable of passing tests for which the presence of boron was thought to be essential to passing.

BACKGROUND OF THE INVENTION

Historically, boron-containing lubricants have been used to attain satisfactory performance against standard industry tests. Two such industry tests are the ISOT and the L60-1. However, boron imparts certain undesirable properties to the lubricant such as moisture sensitivity and increased price. Thus, it is desirable to have a lubricant that can provide the performance demanded by industry while reducing or eliminating the presence of boron. Recently, a boron-free lubricant additive package has been developed that unexpectedly passes both the ISOT standard test and the L60-1 standard test.

SUMMARY OF THE INVENTION

The present invention provides a lubricating additive package that is capable of passing both the ISOT standard test and the L60-1 standard test. More specifically, the present invention in an embodiment provides an oil soluble lubricant additive package comprising: (a) a succinimide dispersant, (b) an antiwear agent, (c) an extreme pressure additive, wherein the weight ratio of said dispersant to said extreme pressure

additive is from about 1:7 to about 1:2, and wherein the package is boron-free, and wherein the total phosphorus content of the package is not more than about 500 ppm.

In another embodiment is provided a lubricating oil comprising: (a) a base oil; and (b) the oil soluble lubricant additive package taught herein.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

In accordance with the foregoing summary, the following presents a detailed description of one embodiment of the invention that is currently considered to be the best mode.

We begin with a discussion of the various components employed in certain embodiments of the present invention. Then we present a lubricant additive package of the present invention and an example of a lubricant oil comprising the inventive lubricant additive package. We conclude with a discussion of the L60-1 and ISOT test performance attained by the inventive lubricant additive package.

BASE OIL

The base oils useful herein include natural lubricating oils, synthetic lubricating oils, and mixtures thereof. Suitable lubricating oils also include basestocks obtained by isomerization of synthetic wax and slack wax, as well as basestocks produced by hydrocracking the aromatic and polar components of the crude. In general, both the natural and synthetic lubricating oils will each have a kinematic viscosity ranging from about 1 to about 40 mm^2/s (cSt) at 100° C, although typical applications will require each of the base oils to have a viscosity ranging from about 1 to about 16 mm^2/s (cSt) at 100° C, preferably 2 to 15 mm^2/s (cSt) at 100° C. Natural lubricating oils include animal

oils, vegetable oils (e.g., castor oil and lard oil), petroleum oils, mineral oils, and oils derived from coal or shale. The preferred natural lubricating oil comprises mineral oil.

The mineral oils useful in this invention can include but are not limited to all common mineral oil base stocks. This would include oils that are naphthenic or paraffinic in chemical structure. Oils that are refined by conventional methodology using acid, alkali, and clay or other agents such as aluminum chloride, or be extracted oils produced, for example, by solvent extraction with solvents such as phenol, sulfur dioxide, furfural, dichlorodiethyl ether, etc. They may be hydrotreated or hydrorefined, dewaxed by chilling or catalytic dewaxing processes, or hydrocracked. The mineral oil may be produced from natural crude sources or be composed of isomerized wax materials or residues of other refining processes. In one embodiment, the oil of lubricating viscosity is a hydrotreated, hydrocracked and/or iso-dewaxed mineral oil having a Viscosity Index (VI) of greater than 80, preferably greater than 90; greater than 90 volume % saturates and less than 0.03 wt. % sulfur.

Group II and Group III basestocks are also particularly suitable for use in the present invention, and are typically prepared from conventional feedstocks using a severe hydrogenation step to reduce the aromatic, sulfur and nitrogen content, followed by dewaxing, hydrofinishing, extraction and/or distillation steps to produce the finished base oil. Also useful herein are base oils known as Group III, $\leq$ 0.03 wt. % sulfur, and $\geq$ 90 vol% saturates, viscosity index > 120; and Group IV, poly-alpha-olefins. Hydrotreated basestocks and catalytically dewaxed basestocks, because of their low sulfur and aromatics content, generally fall into the Group II and Group III categories.

There is no limitation as to the chemical composition of the various basestocks used in the present invention. For example, the proportions of aromatics, paraffinics, and naphthenics in the various Group I, Group II and Group III oils can vary substantially. The degree of refining and the source of the crude used to produce the oil generally determine this composition. In one embodiment, the base oil comprises a mineral oil having a VI of at least 110.

The lubricating oils may be derived from refined, re-refined oils, or mixtures thereof. Unrefined oils are obtained directly from a natural source or synthetic source (e.g., coal, shale, or tar sands bitumen) without further purification or treatment. Examples of unrefined oils include shale oil obtained directly from a retorting operation, petroleum oil obtained directly from distillation, or an ester oil obtained directly from an esterification process, each of which is then used without further treatment. Refined oils are similar to the unrefined oils except that refined oils have been treated in one or more purification steps to improve one or more properties. Suitable purification techniques include distillation, hydrotreating, dewaxing, solvent extraction, acid or base extraction, filtration, and percolation, all of which are known to those skilled in the art. Re-refined oils are obtained by treating used oils in processes similar to those used to obtain the refined oils. These re-refined oils are also known as reclaimed or reprocessed oils and are often additionally processed by techniques for removal of spent additives and oil breakdown products.

Synthetic lubricating oils include hydrocarbon oils and halo-substituted hydrocarbon oils such as oligomerized, polymerized, and interpolymerized olefins; alkylbenzenes; polyphenyls; and alkylated diphenyl ethers, alkylated diphenyl sulfides,

as well as their derivatives, analogs, and homologs thereof, and the like. Preferred synthetic oils are oligomers of α-olefins, particularly oligomers of 1-decene, having a viscosity ranging from about 1 to about 12, preferably 2 to 8, mm^2/s (cSt) at 100° C. These oligomers are known as poly-α-olefins or PAOs.

Synthetic lubricating oils also include alkylene oxide polymers, interpolymers, copolymers, and derivatives thereof where the terminal hydroxyl groups have been modified by esterification, etherification, etc. This class of synthetic oils is exemplified by polyoxyalkylene polymers prepared by polymerization of ethylene oxide or propylene oxide; the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl-polyisopropylene glycol ether having an average molecular weight of 1000, diphenyl ether of polypropylene glycol having a molecular weight of 100-1500); and mono- and poly-carboxylic esters thereof (e.g., the acetic acid esters, mixed C_3-C_8 fatty acid esters, and C_{12} oxo acid diester of tetraethylene glycol).

Another suitable class of synthetic lubricating oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, alkyl succinic acids and alkenyl succinic acids, maleic acid, azelaic acid, subric acid, sebasic acid, fumaric acid, adipic acid, linoleic acid dimer, malonic acid, alkylmalonic acids, alkenyl malonic acids, etc.) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol, diethylene glycol monoethers, propylene glycol, etc.). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) sebacate, di-*n*-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl isothalate, didecyl phthalate, dieicosyl sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebasic acid with two moles of

tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, and the like. A preferred type of oil from this class of synthetic oils is adipates of C_4 to C_{12} alcohols.

Esters useful as synthetic lubricating oils also include those made from C_5 to C_{12} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropane pentaeythritol, dipentaerythritol, tripentaerythritol, and the like.

Silicon-based oils (such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxy-siloxane oils and silicate oils) comprise another useful class of synthetic lubricating oils. These oils include tetra-ethyl silicate, tetra-isopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra-(4-methyl-2-ethylhexyl) silicate, tetra-(p-*tert*-butylphenyl) silicate, hexa-(4-methyl-2-pentoxy)-disiloxane, poly(methyl)-siloxanes and poly (methylphenyl) siloxanes, and the like. Other synthetic lubricating oils include liquid esters of phosphorus containing acids (e.g., tricresyl phosphate, trioctylphosphate, and diethyl ester of decylphosphonic acid), polymeric tetra-hydrofurans, poly-alpha-olefins, and the like.

DISPERSANTS

Dispersants derived from polyisobutylene (PIB) or mixed butane-substituted succinimides are among the succinimide dispersants useful herein, where the molecular weight range of the PIB is approximately 900-2100, most especially MW range 1200-1500. In one embodiment, the succinimide is malienated to a succinic anhydride to PIB ratio of approximately 1.0-1.25. The polyisobutylene succinic anhydride intermediate can be further reacted with a suitable amine including any mono-, di-, or polyamine.

The dispersant may comprise one or more of various types of ashless dispersants including succinimides, succinamides, succinic esters, and succinic ester-amides.

Methods for the production of the foregoing types of ashless dispersants are known to those skilled in the art and are reported in the patent literature. For example, the synthesis of various ashless dispersants of the foregoing types is described in such patents as U.S. Patent Nos. 2,459,112; 2,962,442, 2,984,550; 3,036,003; 3,163,603; 3,166,516; 3,172,892; 3,184,474; 3,202,678; 3,215,707; 3,216,936; 3,219,666; 3,236,770; 3,254,025; 3,271,310; 3,272,746; 3,275,554; 3,281,357; 3,306,908; 3,311,558; 3,316,177; 3,331,776; 3,340,281; 3,341,542; 3,346,493; 3,351,552; 3,355,270; 3,368,972; 3,381,022; 3,399,141; 3,413,347; 3,415,750; 3,433,744; 3,438,757; 3,442,808; 3,444,170; 3,448,047; 3,448,048; 3,448,049; 3,451,933; 3,454,497; 3,454,555; 3,454,607; 3,459,661; 3,461,172; 3,467,668; 3,493,520; 3,501,405; 3,522,179; 3,539,633; 3,541,012; 3,542,680; 3,543,678; 3,558,743; 3,565,804; 3,567,637; 3,574,101; 3,576,743; 3,586,629; 3,591,598; 3,600,372; 3,630,904; 3,632,510; 3,632,511; 3,634,515; 3,649,229; 3,697,428; 3,697,574; 3,703,536; 3,704,308; 3,725,277; 3,725,441; 3,725,480; 3,726,882; 3,736,357; 3,751,365; 3,756,953; 3,793,202; 3,798,165; 3,798,247; 3,803,039; 3,804,763; 3,836,471; 3,862,981; 3,936,480; 3,948,800; 3,950,341; 3,957,854; 3,957,855; 3,980,569; 3,991,098; 4,071,548; 4,173,540; 4,234,435; 5,137,980 and Re 26,433, herein incorporated by reference.

In some embodiments, the ashless dispersant may comprise one or more alkenyl succinimides of an amine having at least one primary amino group capable of forming an imide group. The alkenyl succinimides may be formed by conventional methods such as by heating an alkenyl succinic anhydride, acid, acid-ester, acid halide, or lower alkyl ester with an amine containing at least one primary amino group. The alkenyl

succinic anhydride may be made readily by heating a mixture of polyolefin and maleic anhydride to about 180°-220°C. The polyolefin may be a polymer or copolymer of a lower monoolefin such as ethylene, propylene, isobutene and the like, having a number average molecular weight in the range of about 700 to about 2100 as determined by gel permeation chromatography (GPC).

Amines which may be employed in forming the ashless dispersant include without limitation any that have at least one primary amino group which can react to form an imide group and at least one additional primary or secondary amino group and/or at least one hydroxyl group. A few representative examples are: N-methyl-propanediamine, N-dodecylpropanediamine, N-aminopropyl-piperazine, ethanolamine, N-ethanol-ethylenediamine, N-phenylenediamine, and the like.

Suitable amines may include alkylene polyamines, such as propylene diamine, dipropylene triamine, di-(1,2-butylene)triamine, and tetra-(1,2-propylene)pentamine. A further example includes the ethylene polyamines which can be depicted by the formula $H_2N(CH_2CH_2NH)_nH$, wherein n may be an integer from about one to about ten. These include: ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, and the like, including mixtures thereof in which case n is the average value of the mixture. These depicted ethylene polyamines have a primary amine group at each end so they may form mono-alkenylsuccinimides and bis-alkenylsuccinimides. Commercially available ethylene polyamine mixtures may contain minor amounts of branched species and cyclic species such as N-aminoethyl piperazine, N,N'-bis(aminoethyl)piperazine, N,N'-bis(piperazinyl)ethane, and like compounds. The commercial mixtures may have approximate overall compositions

falling in the range corresponding to diethylene triamine to tetraethylene pentamine. The molar ratio of polyalkenyl succinic anhydride to polyalkylene polyamines may be from about 1:1 to about 2.4:1.

In some embodiments, the ashless dispersant may comprise the products of the reaction of a polyethylene polyamine, e.g. triethylene tetramine or tetraethylene pentamine, with a hydrocarbon substituted carboxylic acid or anhydride made by reaction of a polyolefin, such as polyisobutene, of suitable molecular weight, with an unsaturated polycarboxylic acid or anhydride, e.g., maleic anhydride, maleic acid, fumaric acid, or the like, including mixtures of two or more such substances.

The dispersant may contain at least one polyalkylene moiety. As a further example, the dispersant, may comprise at least two polyalkylene moieties. The polyalkylene moiety may have a molecular weight of from about 900 amu to about 3000 amu. The polyalkylene moiety polyalkylene moiety may, for example, have a molecular weight of from about 1300 amu to about 2100 amu. As a further example, the polyalkylene moiety may have a molecular weight of about 2100 amu. The polyalkylene moiety may comprise a polybutenyl group.

The dispersant may be dissolved in oil of suitable viscosity for ease of handling. It should be understood that the weight percentages given here are for neat dispersant, without any diluent oil added.

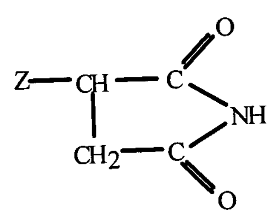
The dispersant may be further reacted with an organic acid, an anhydride, and/or an aldehyde/phenol mixture. Such a process may enhance compatibility with elastomer seals, for example. The dispersant may further comprise a mixture of dispersants. As a further example, the dispersant may comprise nitrogen and/or may be free of phosphorus.

The dispersant may be present in an embodiment in the lubricating fluid in an amount of about 1 wt% to about 5 wt%.

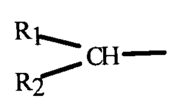
The dispersant used in some embodiments of the present disclosure may comprise a succinimide prepared from an alkenyl succinic acid or anhydride and ammonia. For example, the succinimide may comprise the reaction product of a succinic anhydride and ammonia. The alkenyl group of the alkenyl succinic acid may be a short chain alkenyl group, for example, the alkenyl group may comprise about 12 to about 36 carbon atoms. Further, the succinic anhydride may comprise a C_{12} to about C_{36} aliphatic hydrocarbyl succinimide. As a further example, the succinic anhydride may comprise a C_{16} to about C_{28} aliphatic hydrocarbyl succinimide. As an even further example, the succinic anhydride may comprise a C_{18} to about C_{24} aliphatic hydrocarbyl succinimide.

The succinimide may be prepared from a succinic anhydride and ammonia as described in European Patent 0 020 037, herein incorporated by reference. Further, the succinimide may comprise HiTEC® 3191 friction modifier, available from Ethyl Corporation. In some embodiments, no non-metallic friction modifier other than the succinimide disclosed herein is included.

The succinimide may comprise one or more of a compound having the following structure:



wherein Z may have the structure:



wherein R_1 and R_2 may be independently hydrogen or straight or branched chain hydrocarbon groups containing from about 1 to about 34 carbon atoms such that the total number of carbon atoms in R_1 and R_2 is from about 11 to about 35; and

wherein, in addition to or in the alternative, the succinimide may be formed by reacting maleic acid, anhydride, or ester with an internal olefin containing about 12 to about 36 carbon atoms, said internal olefin being formed by isomerizing the olefinic double bond of a linear α-olefin or mixture thereof to obtain a mixture of internal olefins.

One embodiment utilizes a poly-amine of the type tetra ethyl pentamine. Examples can include but are not limited to HiTEC® 646 Dispersant, available from Ethyl Corporation, and similar succinimide dispersants.

EXTREME PRESSURE ADDITIVES

Extreme pressure agents known to those skilled in the art are useful in the lubricant additive packages, lubricating oil, lubricated machines, and methods of the present invention. Also useful herein as extreme pressure agents are sulfurized olefins, including but not limited to sulfurized isobutylene, alkylpolysulfides and sulfurized fatty acid esters.

CORROSION INHIBITORS

Corrosion inhibitors of the thiadiazole and triazole classes are suitable for use in this invention. Alkyl substituted thiadiazoles as well as alkyl substituted triazoles are useful in this invention.

OTHER AGENTS

Antiwear and siloxane-containing polymer antifoam agents, well known to those skilled in the art and as taught in, for example, U.S. Patent No. 5,492,638, can also be employed in the lubricant additive packages and finished lubricating oils of the present invention.

A variety of oil-soluble sulphur-containing antiwear and/or extreme pressure additives can be used in the practice of this invention. Examples are included within the categories of dihydrocarbyl polysulphides; sulphurized olefins; sulphurized fatty acid esters of both natural and synthetic origins; trithiones; sulphurized thienyl derivatives; sulphurized terpenes; sulphurized oligomers of C2 -C8 monoolefins; and sulphurized Dieis-Alder adducts such as those disclosed in U.S. reissue patent Re 27,331. Specific examples include sulphurized polyisobutene of Mn 1,100, sulfurized isobutylene, sulphurized diisobutylene, sulphurized triisobutylene, dicyclohexyl polysulphide, diphenyl polysulphide, dibenzyl polysulphide, dinonyl polysulphide, and mixtures of di-tert-butyl polysulphide such as mixtures of di-tert-butyl trisulphide, di-tert-butyl tetrasulphide and di-tert-butyl pentasulphide, among others.

Combinations of such categories of sulphur-containing antiwear and/or extreme pressure agents can also be used, such as a combination of sulphurized isobutylene and di-tert-butyl trisulphide, a combination of sulphurized isobutylene and dinonyl trisulphide, a combination of sulphurized tall oil and dibenzyl polysulphide, and the like.

Reference should be had to EP 531 585 referred to above for further details concerning this component.

For purposes of this invention a component which contains both phosphorus and sulphur in its chemical structure is deemed a phosphorus-containing antiwear and/or extreme pressure agent rather than a sulphur-containing antiwear and/or extreme pressure agent.

One such type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additives which can be employed in the practice of this invention are the

phosphorus- and nitrogen-containing compositions of the type described in G.B. 1,009,913; G.B. 1,009,914; U.S. Pat. No. 3,197,405 and/or U.S. Pat. No. 3,197,496. In general, these compositions are formed by forming an acidic intermediate by the reaction of a hydroxy-substituted triester of a phosphorothioic acid with an inorganic phosphorus acid, phosphorus oxide or phosphorus halide, and neutralizing a substantial portion of said acidic intermediate with an amine or hydroxy-substituted amine.

Another type of phosphorus- and nitrogen-containing antiwear and/or extreme pressure additive which can be used in the compositions of this invention is the amine salts of hydroxy-substituted phosphetanes or the amine salts of hydroxy-substituted thiophosphetanes. Examples of this general type of antiwear and/or extreme pressure agent include the amine salts hydroxyphosphetanes and the amine salts of hydroxy-thiophosphetanes typified by Irgalube 295 additive (Ciba-Geigy Corporation).

Another useful category of phosphorus- and nitrogen-containing antiwear and/or extreme pressure agents is comprised of the amine salts of partial esters of phosphoric and thiophosphoric acids. For further details concerning this component, reference should be had to EP 531 585 referred to above.

The formulations of the present invention have a total phosphorus content of not more than about 500 ppm. The formulations are also boron-free. By "boron-free" herein is meant substantially free of boron whereby trace amounts of or contamination with low or unintended levels of boron are to be included. Boron-free can herein include low levels of boron up to about 25 ppm. By "substantially free of boron" herein is meant less than about 50 ppm of boron.

NOTE: Current Boronated packages offered by Ethyl contain 125 – 150ppm of Boron. I think the above levels are too high

EXAMPLE FORMULATION

An example of an oil soluble lubricant additive package formulation of the present invention is outlined in the table below:

Component	**Wt %**
Sulfurized olefin	30-50
Primary amine	0.1 - 5
Acid phosphate	0.5 – 5.0
Rust Inhibitor	0.01 - 1
Antifoamant	0.2 – 2.0
Corrosion Inhibitor	0.2 – 2.0
Diluent Oil	30 - 40
Dispersant	2 – 15.0

A finished oil comprising the preferred boron-free oil soluble lubricant additive package was manufactured for testing purposes. The finished oil was then tested by the L60-1 and the ISOT standard tests. It was unexpected that a lubricant additive

package could pass both the L60-1 and ISOT standard tests without the inclusion of a boron source in the formulation.

	Dispersant	Phosphorus	Boron	L-60-1		ISOT	
		ppm	ppm	C / V	Sludge	Beaker	Rod
Additive							
Package A	Yes	1,425	158	9.25	9.59	2.5	1
Package B	Yes	870	132				
Package C	Yes	680	0			8.0	9.0
Package D	Yes	576	150	9.10	9.64	2.0	2.0
Package E	Yes	525	195	9.10	9.54	2.5	2.5
Package F	Yes	525	0	8.15	9.50	[redacted]	[redacted]
Package G	NO	525	0	3.40	8.68	7.0	9.0
Package H	NO	300	0	7.60	9.46	8.0	9.0
Invention	Yes	300	0	9.44	9.52	1.5	2.0

The L60-1 test requires at least a 7.5 carbon / varnish (C / V) rating or higher to pass, and at least a 9.4 sludge rating or higher to pass. The L60-1 rating is based on a merit system with 10 indicating no carbon / varnish and zero representing the worst rating.

The ISOT test, conversely, requires at most a 3.0 for varnish on the glass beaker and for varnish on the glass rod to indicate clean gear performance. The ISOT rating is based on a demerit system with the best ISOT rating zero indicating no varnish and 9 representing the worst varnish rating. This rating may also be described as thinly to lightly adhering lacquer in the ISOT procedure. Note that prior art formulations containing phosphorus and boron pass both tests. Formulations with low phosphorus

alone do not pass both tests. Only the formulations of the present invention with both low phosphorus and a dispersant pass both tests without boron.

The formulations of the present invention are especially effective in the lubrication of vehicular axle gears and vehicular transmission gears. The vehicles can be passenger cars, light duty trucks, heavy duty trucks, buses, recreation vehicles, marine craft, and the like.

While the invention has been described in connection with what is presently considered to be the most practical and preferred embodiments, it is to be understood that the invention is not to be limited to the disclosed embodiment(s), but on the contrary, is intended to cover various modifications and equivalent arrangements included within the spirit and scope of the appended claims, which are incorporated herein by reference.